

ADHESION AND LEVELING IMPROVEMENT OF SILOXANE POLYMER
COATINGS ON POLYIMIDE AND POLY(METHYL METHACRYLATE)

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ABSTRAKTI

Joka vuosi käytetään valtava määrä muoveja, joten huonon ympäristövaikutuksen vähentämiseksi muovien käyttöä pyritään pidentämään suojaavilla pinnoitteilla. Siloksaanipolymeeripinnoitteet ovat osoittaneet kovaa abraasikestävyyttä suojaamalla esimerkiksi polyimidi- ja polymetyylimetakrylaattipintoja. Hyvän pinnoitteen saavuttamiseksi kahden pinnoitemateriaalin ominaisuuden, pinnoitemateriaalin tasoittumisen pinnoitettavalle alustalle sekä adheesion eli pinnoitemateriaalin tarttumisen pinnoitettavaan alustaan, tulee toimia kunnolla. Tähän pro gradu tutkielmaan on kerätty tuloksia eri tieteellisistä lähteistä, esimerkkejä ja menetelmiä, joiden avulla voidaan parantaa pinnoitteen adheesiota ja tasoittumista polyimidille ja polymetyylimetakrylaatille. Tässä työssä tarkastellaan, mitä vaikutuksia adheesioon ja tasoittumiseen on esimerkiksi substraatin rakenteella, esikäsitteily- ja pohjakäsittely menetelmillä sekä pinnoitemateriaalin koostumuksella, esimerkiksi eri polymeereillä ja lisäaineilla. Lopuksi työssä tarkastellaan myös erilaisten pinnoitusmenetelmien vaikutusta tasoittumiseen.

ABSTRACT

Massive amounts of plastics are used every year, and to decrease their negative environmental impact the aim is to prolong their service life by using protecting coatings. Siloxane polymer coatings show hard abrasion resistance in protecting for example polyimide and poly(methyl methacrylate) surfaces. For good coating performance the two coating properties need to be working properly, the leveling of coating material to the substrate and the adhesion of the cured coating to the substrate material. This Master thesis collects results from different scientific sources, examples, and procedures how to improve adhesion and leveling on polyimide and poly(methyl methacrylate). This thesis considers the different effects on adhesion and leveling for example due to the substrate structure, pre-treatment and priming methods, and coating material composition with different polymers and additives. At the end, also the effect of coating method to leveling is considered.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	i
ABSTRAKTI.....	ii
ABSTRACT	iii
TABLE OF CONTENTS	iv
ABBREVIATIONS	v
1. INTRODUCTION	1
2. ADHESION AND LEVELING AS PHENOMENA	4
2.1. Adhesion	4
2.2. Leveling	6
3. ANALYSIS METHODS	10
3.1. Analysing adhesion.....	10
3.1.1. Surface characterization techniques	10
3.1.2. Mechanical inspection of adhesion of coatings	11
3.2. Analysing leveling	15
4. IMPROVING OF ADHESION	19
4.1. Adhesion on PI.....	21
4.1.1. Structure of PI.....	21
4.1.2. Improving of adhesion on PI	23
4.2. Adhesion on PMMA	26
4.2.1. Structure of PMMA	26
4.2.2. Improving of adhesion on PMMA	27
5. IMPROVING OF LEVELING.....	32
5.1. Controlled leveling	33
5.2. Coating methods effect on leveling	35
5.3. Improving of leveling on PMMA	39
6. CONCLUSION	42
7. REFERENCES	44

ABBREVIATIONS

AFM	Atomic force microscopy
AO	Atomic oxygen
APTES	γ - Aminopropyltriethoxysilane
ATR-IR	Attenuated total reflectance infrared spectroscopy
FT-IR	Fourier transform infrared spectroscopy
MTMS	Methyltrimethoxysilane
PC	Polycarbonate
PET	Poly ethylene terephthalate
PECVD	Plasma enhanced chemical vapour deposition
PI	Polyimide
PMMA	Poly(methyl methacrylate)
PTMS	Phenyltrimethoxy silane
SEM	Scanning electron microscopy
SFG	Sum frequency generation, vibrational spectroscopy
ToF-SIMS	Time-of-flight secondary ion mass spectrometry
TEOS	Tetraethoxysilane
UV	Ultraviolet
WCA	Water contact angle
XPS	X-ray photoelectron spectroscopy

1. INTRODUCTION

Plastics are of great industrial interest due to their versatility of utilization. According to the Finnish Plastics Industries Federation, plastics are needed practically in all vital functions of society; household items, automotive parts, transporting and protecting for clean water, grocery, and other commodities. Annually, 600 000 tons of plastics are used to make different products only in Finland. Advantages of plastics are low density, energy efficiency, low cost, ease of manufacture and moldability to almost any purpose. [1] Plastics like polyimide (PI) and poly(methyl methacrylate) (PMMA) have poor durability due different environmental effects and scratching easily, resulting to shorter lifetime of the final product. One of the key activities to improve the plastic long-term usability is to add protective coating on top of plastic which has direct effect to environmental impact.

A thin material layer called coating is meant for protective or decorative purposes onto different surfaces. Coatings are widely used in different industrial areas, for example as protection against corrosion, weather, and impact on transportation vehicles (ships, cars), houses, and household items like ceramics, device screens, kitchen appliances etc. Mostly the coating is wanted to be permanent, but there are also strippable coatings for shorter periods. [2, p. 430] Because the coating material is attached to the substrate surface, the coating material must vary depending on the chosen substrate. Coating compositions are specified for, e.g., different metals and plastics. Composition of both the substrate and the coating affects the chemical reactions in their interface, and thus affects the product performance.

As a process coating means spreading of a thin uniform layer of liquid-phase coating material onto a substrate [3]. There are different methods to spread the coating material, and different coating methods have an effect for example on coating thickness and smoothness. To achieve the best performance of coating for the end product, the coating surface must be even, defect-free, and permanently attached to the substrate. Phenomena behind good clinging and uniform coating surface are adhesion and leveling, respectively.

Problems with adhesion can occur already in the processing state, when just outspread coating does not attach to the substrate. Even if the coated product is ready, sooner or later the coating can detach due to poor adhesion or ageing and environmental effect on either one or both of the coating and the substrate, leading to poor product performance and

possibly short lifetime of the product. Problems with leveling in the processing state can be seen immediately if the coating material does not spread; it gets lumpy or withdraws itself to droplets on the surface, and not level at its place smoothly as it is meant. Leveling problems are also detected afterwards, when the cured coating surface looks smooth to the eye, but in testing the surface still has roughness, for example stripes from bar coating technique etc. Rough or uneven coating surface in moving parts or device screens wears out unevenly, and also leads to poor end product performance or short lifetime.

The aim of this work is to consider different siloxane polymer coating materials, different material components, the reactions of siloxane polymers on different plastic substrates in terms of adhesion and leveling, and the environmental effects on adhesion. Siloxane polymer coatings are of great interest for several properties. According to IUPAC, siloxane is defined as saturated hybrids of alternating silicon and oxygen atoms with unbranched or branched chains, where oxygen atoms separates each neighbouring silicon atom. [4] The higher Si-O bond energy compared to that of carbon main chain provides exquisite thermal stability for siloxane coatings. Flexibility of this polymer in wide temperature range from -60°C to 250°C is due to the high bond angle of Si-O-Si chain causing easy free rotation. Siloxane polymers are more suitable for coating purposes compared to other polymers due their low surface tension, commonly about 22 mN/m, which leads to good material spreading. [5] Coating composition, siloxane polymer, and different additives have their own effect on adhesion and leveling, and those will be reviewed in this thesis.

In this thesis, adhesion and leveling of siloxane coatings are reviewed in view of PI and PMMA as substrates. Wider variety of commercial products can be achieved by using different substrates, and chemical and physical structure of the substrate contribute to both adhesion and leveling phenomena. Polyimides are well-known as polymeric material with remarkable thermal stability. Originally, high heat-resistance polymers, including polyimides, were developed for the needs of aerospace demand. Nowadays, especially PIs with their high compressive strength and flexural modulus are widely commercially used in both automotive and aircraft structures. [6, p. 186] Despite its overall phenomenal performance, PI is sensitive to attacks of alkalis and acids, and other environmental effects. [7] Especially, the degrading effect of atomic oxygen in open atmosphere environment is significant, which can be mitigated by coated surface. [8]

PMMA has great variety of use, for example in signs and architectural structures, taillights for cars and optical fibres for light transmission. PMMA is an economical substitute to polycarbonate (PC) if high toughness and impact resistance are not needed. [9] PMMA has good resistance against oils, alkanes, and diluted acids, but poor resistance against several polar solvents. It is quite friable material and has weak impact resistance, which can be improved by addition of toughened acrylics or by coating the surface.

2. ADHESION AND LEVELING AS PHENOMENA

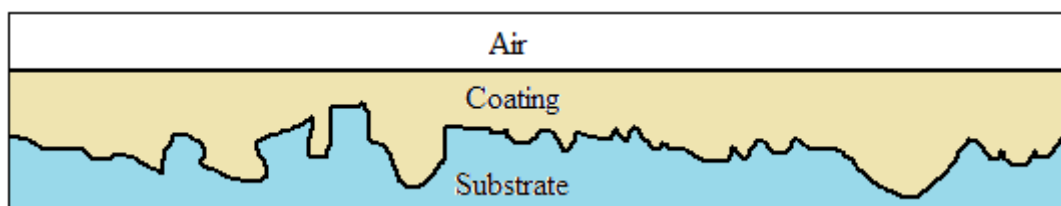
Adhesion and leveling as properties are often in significant role for desired performance of commercial products. This chapter will narrate the meaning of the phenomena, their mechanisms, and what is the impact of coating, substrate, and environment on these phenomena.

2.1. Adhesion

Adhesion is the interaction at the interface between atoms and molecules of two surfaces making them stay attached. Though in this thesis the focus is on adhesion of siloxane polymer coatings on plastics, adhesion as phenomenon in wider perspective occurs also in other industrial fields, for example at the cell level at biomedical industry and tissue engineering, adhesion of proteins etc. [10], and for example in wastewater cleaning processes, adhesion of particles from liquid to surface [11]. Most of the existing materials can be bonded, at least with adhesive bonding or through cohesion between similar particles, but adhesion has also an opposite phenomenon, abhesion, avoiding bonding between two materials. Abhesion is desirable in non-sticking surfaces of materials like polytetrafluoroethylene, commercially called Teflon. [12, p. 25] Abhesion is not further reviewed in this thesis.

There are different types of adhesion mechanisms recognized in past decades. Main adhesion types are named mechanical coupling, chemical or molecular bonding, and adhesion based on thermodynamics. Also, rheological and electrical adhesion affects the adhesion as a whole. [10] So called adhesive bonding occurs when a material layer called adhesive is added between the two surfaces, substrate and adherend, to bind them together. Adhesive bonding can ease adhesion especially between very dissimilar materials [10], but this is not usually used with liquid coating materials.

Mechanical adhesion occurs when initially liquid coating material penetrates the substrates porous surface before being hardened and then works as fastener. The mechanical interlocking, shown in Picture 1, prevents the coating from sliding or moving horizontally on the substrate. Chemical adhesion is based on secondary forces between two binding impermeable, non-porous, surfaces. Molecular bonding includes van der Waals forces, dipole-dipole interactions, and chemical interactions, meaning covalent, ionic, and metallic bonding. [2]



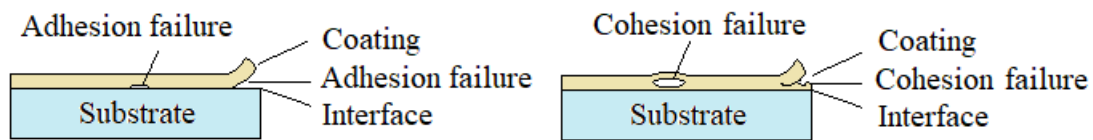
Picture 1. Illustration of mechanical interlocking of a coating onto a substrate.

According to thermodynamic adsorption model of adhesion, the polymer system in neutral environment tends to minimize its surface free energy, by orientating the surface towards the non-polar section of the polymer. When being in touch with polar material, for example water, it is important to minimize the interfacial tension to achieve good adhesion. One of advantages of thermodynamic mechanism is that molecular interaction is not necessary for good adhesion, but equilibrium process at the interface is required. Water contact angle represents the thermodynamic model of adhesion and will be discussed in Chapter 3.1.2. [10]

The rheological mechanism of adhesion occurs due to interpenetration of substrates across their interface. For example, heating the polymers over their glass transition state allows strong adhesive bond formation due to increased polymer chain mobility. The electrical mechanism of adhesion occurs when two joining materials have different band structures at the interface, so that there is mutual electron sharing during contact. [10]

Properties and mechanisms of interfacial adhesion are dependent on the buried interfaces molecular structure. [13] In addition to adhesion mechanisms, internal stresses of system influence the adhesion strength. The internal stresses depend on relaxation processes when polymeric coatings are forming alongside with uneven curing of coating, interactions with surface of solid, and temperature gradient if present. Internal stresses' effect is related to the rheological adhesion mechanism. Furthermore, the first few atomic layers by both chemical and physical configuration defines the adhesion and other polymer properties, but the layer just below, the subsurface, controls the outer layer too. The subsurface mobility, in both coating and substrate materials, is restrained by crosslinking and double bonds, which stabilize the functional groups at the outer layer. [10]

Adhesion failures in coatings should not be confused with cohesion failures, illustrated in Picture 2. Adhesion failure is in the interface and the failure is in bonding between coating material and substrate, while cohesion failure is malfunction of the cured coating material itself.



Picture 2. Illustration of adhesion and cohesion failures in coating-substrate interface.

Environment affects coating's adhesion through ageing, and degradation is usually the consequence of UV irradiation, high or variable temperature, and moisture. Polymer degradation is caused by both chemical and physical processes, and both processes can lead to coatings that crack and/or detach from the substrate, though physical processes are less well known because of their complexity. Environmental effects should be analysed from both coating and substrate to understand the effect to adhesion at the interface since the degradation effect can differ between coating and substrate. [14]

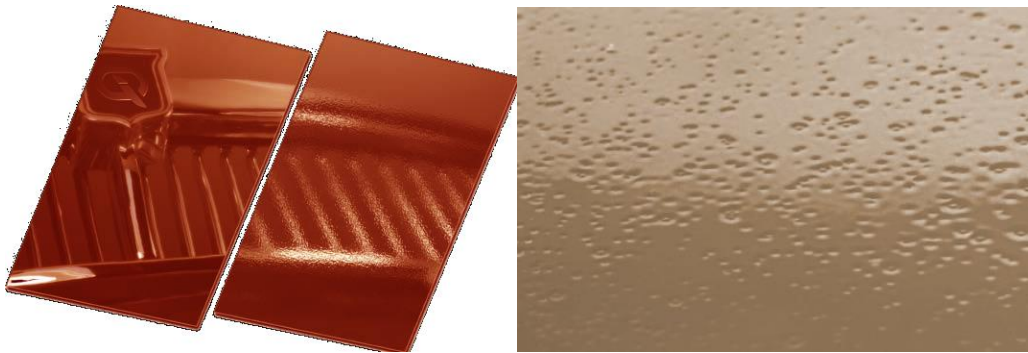
2.2. Leveling

Leveling is a property of liquids to set on their place and equalize thickness at a surface. Leveling as a phenomenon can be found in different industrial fields, for example cement and concrete surfaces, fingernail polishes, and all kinds of paints and coatings. [15] [16] In this thesis, the focus is on leveling of siloxane polymer coatings on plastic surfaces.

In paintings and coatings, visual quality is important, but also several other coating properties, e.g., mechanical stability and water contact angle depend on how smooth and uniform the coating surface is. To achieve consistent coating, the coating material and all its flaws should be leveled before the coating dries. The studies of leveling of disturbances should take into account the surface tension, viscosity and drying of the coating material, Marangoni-effect, gravity, and elasticity. [3] Picture 1 is also showing the ideally leveled coating, which refines the outer surface by covering the substrate roughness. Leveling is driven by surface tension alongside with gravity and capillarity, but it can also be altered for example by changing charge distribution or changing the structure of the coating material.

When the coating material is applied to the substrate, for example by bar coating, leveling should flatten the surface thickness between valleys and peaks. Usually leveling flow is directed from valleys to peaks, but Marangoni-effect describing the surface tension gradient turns the initial peaks into valleys and *vice versa*. In this so-called reversal process flow is directed from peaks to valleys and it is enhancing the overall leveling process. [17]

Problems with leveling are mostly visible, though other analysis methods are also needed, and those methods are described in Chapter 3.2. Visually detectable issues can be divided by their appearance, and they can occur in wet or dry films as orange peel and fisheyes effects, bubbles, pin holes, craters, so-called Bernard cells, popping, stripes after bar coating, crawling from film into droplets etc. In Picture 3, the two coated sheets on the left represent well levelled coating (on the far left) against one with orange peel effect. The uneven matte orange peel effect is common especially when coating material is sprayed on the substrate. In Picture 3, the coated surface on the right has visible craters; wide holes in partly smooth surface. Craters or pinholes are caused by contamination, liquid or solid traces of something with highly different surface tension than the coating material. Craters and pinholes look quite the same, except that pinholes are narrower. Instead of solid contamination, pinholes can also have gas or air-void inside. They can also have non-homogenous liquid layer creating pressure difference and dent. [16] Pinholes differ from bubbles in that bubbles usually stay on top of the coating, but pinholes go through the coating layer.



Picture 3. On the left levelled coating and the orange peel effect, craters on the right. [16]

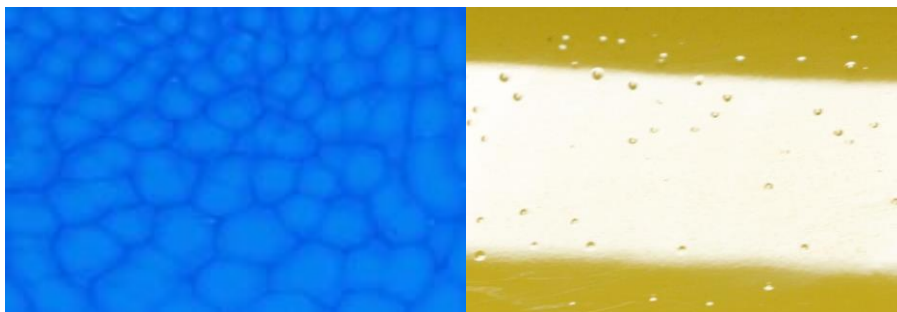
The “fisheyes” and crawling or dewetting effects are shown in Picture 4. The fisheye effect occurs due to inadequate wetting of the surface, caused by significantly lower surface tension of substrate than that of the liquid coating, and no spreading occurs. Dewetting or crawling is similar, and it appears when the coating seems to wet the substrate surface, but during or shortly after coating addition it retreats or pulls back due to lack of stability at the substrate-coating interface.



Picture 4. The fisheyes effect on left and crawling/dewetting effect on the right. [16]

In paintings but also seen on clear coatings, so called Bernard cells, shown on left in Picture 5, form from turbulent flow of coating material caused by differences in surface tension and density. Flow direction is from the lower to the upper part of the coating material layer. Larger molecules of the material, additives, or pigment in paints, settle differently depending on their mobility on the surface area, and form pattern seen with hexagonal shape on horizontal substrate. On the other hand, in vertical substrate, the same effect takes more line-shaped pattern. [16] Even in clear films, if the material distribution is not uniform due flow differences, the denser areas can be visible.

All leveling issues mentioned above are usually visible already on wet film soon after coating but are also seen in dry films. On the left in Picture 5, a leveling issue called popping or dimpling is visible. It is caused by the release of trapped volatiles like solvent during baking or curing process, when outer layer is already set but some volatile bursts out from the coating layer leaving hollow markings.



Picture 5. Bernard cells on left and popping on right. [16]

Some trapped gas can also come from the substrate, or if waterborne primer is used, dehydration in primer layer can destroy the top coating, which is then seen as coating leveling failure. Also, if overspray is used, it can absorb solvent from subsequent coating layers, or the spraying itself can trap some solvent which is then popping out from the outer

layer. Popping, or also called gassing, can be difficult to distinguish from craters, bubbles, or pinholes. [16]

3. ANALYSIS METHODS

To understand adhesion and leveling as phenomena, and to improve them in commercial applications, it is important to obtain information from the coating, substrate, and their interface. Both chemical and physical composition and structure are affecting the phenomena, and they give clues on what reactions occur in the interface of coating and substrate, and how those reactions are driving adhesion and leveling to better or worse. This chapter will give an overview on different methods to analyse both adhesion and leveling.

3.1. Analysing adhesion

Adhesion can be analysed in multiple ways. Different surface characterization techniques disclose chemical and physical structure and composition of surface or interface to indirectly characterize adhesion. Strength of adhesion and mechanical performance can be studied directly with different equipment either destructively or non-destructively.

3.1.1. Surface characterization techniques

There are several techniques that can be used for surface characterization regarding to indirect adhesion mechanism and strength studies. For example, techniques like time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), secondary electron microscopy (SEM), attenuated total reflectance infrared spectroscopy (ATR-IR) or Fourier transform infrared (FT-IR) provide important information from surface properties. Surfaces chemical composition, roughness, polarity, and surface free energy are important properties that dictate adhesion phenomenon at a surface or interface. [5]

ToF-SIMS instruments provide mass spectra under clean ultrahigh vacuum conditions. With high surface sensitivity ToF-SIMS generates elemental, isotopic, and molecular information of a surface monolayer. This information describes the chemistry at the interface, giving understanding of adhesive reaction. XPS generates spectrum of photoelectron intensity shown as function of binding energy, presenting the electronic structure of the analysed beamed atoms to around 5 to 10 nm depth at the surface. The peaks of the spectrum are characteristic and so identify the species and quantify the relative composition of the surface. XPS also facilitates quantitative correlations between surfaces elemental or functional groups and surface energy or adhesion strength. ATR-IR is also used for molecular

characterization of surfaces. For example, it can detect bonds between nitrogen and substrate after N₂ plasma treatment.

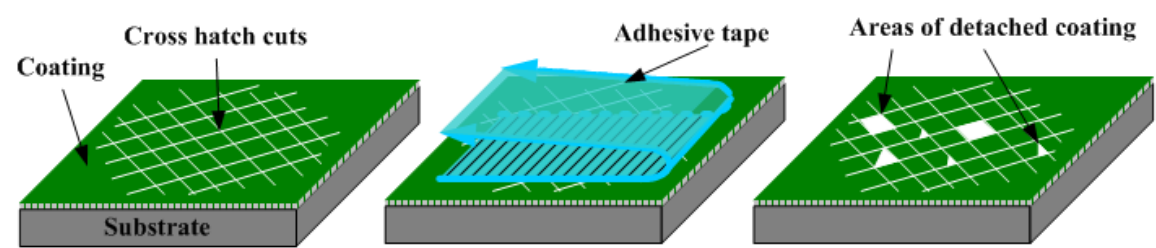
AFM provides a topographic map of the surface showing cantilever deflections as a function of parallel scanning lines. Deflections are formed by interaction with the surface. AFM has usually atomic resolution allowing it to detect changes in topography also from treated surfaces, giving information how surface roughness contributes to adhesion strength. SEM provides also topographic information, using electron scattering. SEM's resolution may achieve few nanometer spatial resolution and relatively wide range in depth. This topographic information tells us about the reactions between the substrate and the surface treatment. [5]

In study of Myers and Chen, sum frequency generation (SFG) vibrational spectroscopy was used for interfacial studies between polyimide/air and polyimide/epoxy adhesive interfaces. SFG is a non-destructive characterization technique used to obtain information from molecular structures of buried polymer interfaces, including information about adhesion, together with interfacial water transport and interaction energy. [13] When studying chemical degradation, ageing, and environmental effects on coatings, for example FT-IR and XPS are used to detect changes in chemical composition and deterioration of chemical stability. [14]

3.1.2. Mechanical inspection of adhesion of coatings

Mechanical performance of adhesion can be studied in different ways, especially depending on the system under inspection, but here the focus is on studying adhesion of coatings on a substrate, not for example adhesion between two substrates. Many mechanical adhesion testing techniques are destructive to the coatings. For example, an international company Elcometer® provides among other things inspection equipment for coating testing. For adhesion testing, they have equipment for pull off, push off, cross hatch adhesion testing, and a unit of adhesion verification. All of these testing methods are direct and destructive, and they measure the needed force for breaking, tearing, or delaminating a coating at the interface, or the amount of damage caused by specific testing style, like cross hatch test. So-called pull off adhesion test equipment uses an adhesively attached dolly, which then pulls off the coating when the dolly is lifted. Adhesion strength is given as a value of force per area unit needed to lift the dolly. Elcometer's adhesion verification unit is an automatic device based on pull off adhesion testing. Push off adhesion test defines the required pressure

to push away a certain area of coating from substrate. Cross hatch adhesion testing with pull-off tape test works according to ASTM standard D3359 and ISO2409, and it is illustrated in Picture 6. Adhesion results using crosshatch and tape test are given in scale introduced more detailed in Table 1. [18] [10]



Picture 6. Illustration of cross hatch adhesion test. [19]

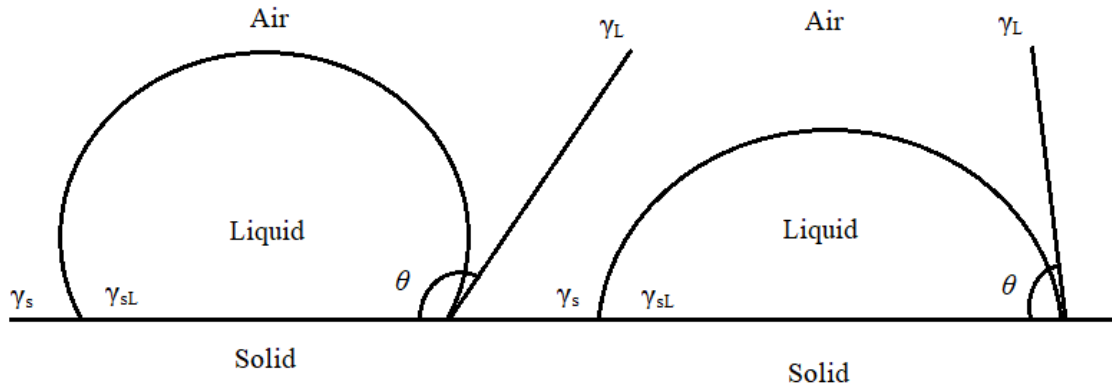
Table 1. Classification of adhesion test results, standard D3359 and ISO2409

Illustration of damaged area	% of area removed	Standard	
		ISO2409	D3359
	None	0	5B
	< 5%	1	4B
	5–15%	2	3B
	15–35%	3	2B
	35–65%	4	1B
	> 65%	5	0B

One non-destructive mechanical property analysing technique is measuring contact angle. Water contact angle (WCA) of a coating tells us about a coating’s hydrophobicity,

wettability, and easy-to-clean effect. The higher the WCA value, the better the easy-to-clean effect is, which requires also good leveling.

Contact angle of liquid coating material tells about adhesion to the substrate due work of adhesion. Contact angle represents the thermodynamic adhesion mechanism, meaning that the higher the CA, the better minimized the interfacial tension is. Picture 7 illustrates CA of two different sessile drops in a simple system. The sessile drop on left has CA close to 120° and the sessile drop on right has CA close to 80° . The system is considered to have a liquid with a known surface tension and a simple solid with a smooth, uniform, non-deformable, and isotropic surface. [10] Surface tension measurement will be reviewed in more detailed in the next chapter, 3.2. Analysing leveling.



Picture 7. Contact angle measurement. [2]

With as simple systems as shown in Picture 7, the strength of adhesion may be estimated through the thermodynamic work of adhesion, W_a , which is defined as

$$W_a = \gamma_s + \gamma_L - \gamma_{sL} \quad (1)$$

where γ_s , γ_L , γ_{sL} represent the tensions of the solid/air, liquid/air and solid/liquid interfaces, respectively. The challenge with this equation is that only γ_L can be measured with confidence as the surface tension of the solid can only be experimentally determined against a series of known liquids. The relationship between these three is required and it can be described with equation:

$$\gamma_L \cos \theta = \gamma_s - \gamma_{sL} \quad (2)$$

Now it is possible to derive, by substitution from equation (1) and equation (2), the work of adhesion by γ_L as equation:

$$W_a = \gamma_L(1 + \cos \theta) \quad (3)$$

CA, θ , can be measured using optical tensiometer. Numerical values for W_a can be then calculated based on equation (3). [10]

If this thermodynamic work of adhesion has a positive value, the bond is stable. Conversely, unstable bonding occurs even in stressless conditions with a negative work of adhesion values. The work of adhesion has been studied with presence of water especially to predict durability of adhesive bonding joint. [12, p. 111]

In the study of Dorrnanian et al., they divided the surface tension of solid-liquid interface γ_s further into the intermolecular attraction of polar interaction γ_s^p and the dispersion interaction γ_s^d , so that

$$\gamma_s = \gamma_s^p + \gamma_s^d \quad (4)$$

For water, the surface tension γ_s is 72.8 mN/m, γ_s^p is 51.0 mN/m, and γ_s^d is 21.8 mN/m. In the context of liquids, it is sometimes more convenient to consider the surface tension rather than the surface energy. The surface energy is still related to the surface tension through unit review, because

$$\text{Surface energy} = \frac{\text{Energy}}{\text{Area}} \quad (5)$$

$$\begin{aligned} &= \left[\frac{\text{Joule}}{\text{m}^2} \right] = \left[\frac{\text{Newton} \cdot \text{m}}{\text{m}^2} \right] = \left[\frac{\text{Newton}}{\text{m}} \right] \\ &= \frac{\text{Force}}{\text{Lenght}} \end{aligned} \quad (6)$$

Surface tension can also be defined as

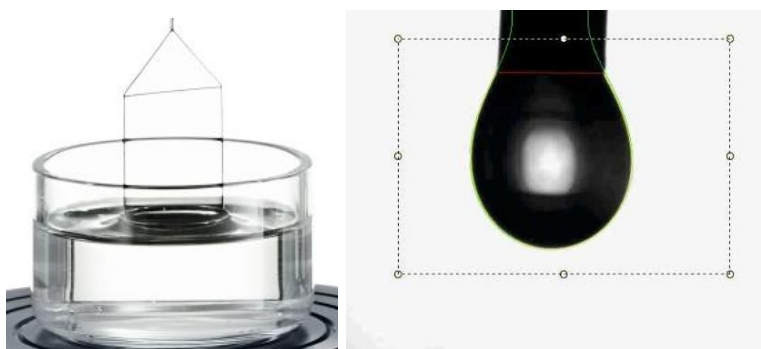
$$= \frac{\text{Force}}{\text{Lenght}} \quad (6)$$

The surface energy studies of Dorrnian et al. on PMMA will be reviewed later in chapter 4.2.2. [20]

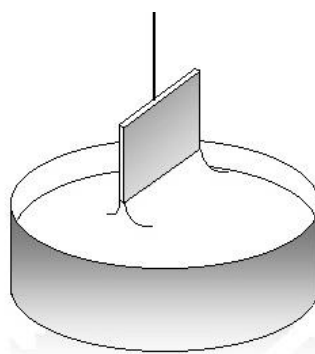
When moving from simple systems to real systems, contact angle measurement is not that straightforward. Macroscopic surface roughness and diversity in chemical structure can cause contact angle hysteresis: larger contact angle is measured when test fluid expands the sessile drop and covers larger surface than measured when the sessile drop retreats. To achieve a wider understanding of polymer adhesion in a specific application, it is recommended to use a combination of direct measurement, CA, and surface characterization techniques like XPS and ToF-SIMS. [10]

3.2. Analysing leveling

Leveling and movement of liquid materials can be studied and predicted before it is cured. Surface tension of the coating material and the substrate, and the difference in these tensions, is important to understand for making improvements to the material composition. Surface tension of a liquid is traditionally measured with the Du Noüy ring or the Wilhelmy plate, but it can also be measured with a pendant drop in air. [21] Picture 8 shows a Du Noüy ring on left and pendant drop on right. Illustration of the Wilhelmy plate is shown in Picture 9.



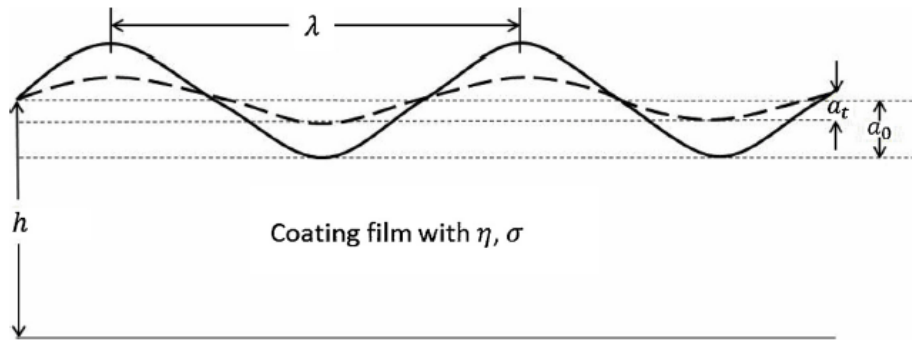
Picture 8. Du Noüy ring on left and pendant drop on right. [22]



Picture 9. Illustration of Wilhelmy plate. [23]

Pendant drop is based on calculating surface tension from the angle of the upper part of constant volume drops of different liquids. The smaller angle refers to stronger tension and higher angle to weaker tension. The Du Noüy ring and Wilhelmy plate methods are based on measuring force needed to pull the ring or plate through the liquid surface. Relation between surface tensions and contact angles was described on page 13, but in addition to that, using polymer liquids, including additives instead of pure solvents, will complicate and change both surface tensions of the solid/liquid and the liquid/air interfaces and result in a different contact angle. [24] Making conclusions based on solely the contact angle can lead in the wrong direction in coating material development. Viscosity of the liquid coating material affects the flow and leveling of the material. Viscosity of a fluid is commonly measured with a viscometer.

Wang et al. studied the leveling with wide-area 3D profilometer containing optical VR-3100 sensor from KEYENCE. They scanned surfaces of solvent-containing coating and obtained information about the dynamic surface texture. Texture includes information about waviness (macro-roughness) and roughness (micro-roughness), whose wavelength differs in scale. [17] [25] Wang et al. also used ISO 25178-2 standard to evaluate their results. In leveling studies, a well-defined sinusoidal surface structure can be generated to better study significant leveling parameters. These parameters used in studying both wet and dry film leveling as both mathematical and experimental methods are introduced in more detail in Picture 10.



Picture 10. Illustration of sinusoidally levelled coating with different parameters. [25]

These parameters shown in Picture 10 are the viscosity η (Pa·s), surface tension σ (N/m), wavelength λ (m), average film thickness h (m), amplitude a_0 at the time 0 (m) and amplitude a_t at given time t (m).

Analysing leveling can be done also after the coating material is cured. ISO 25178-2 standard describes several areal surface texture parameters from three categories, using field, feature, and functional parameters. Surface profile parameters have been described earlier via other standards, but the most recently published ISO 25178-2 standard introduced first the areal parameters, and these parameters are more widely used in industrial and scientific studies in the place of profile parameters. The areal surface parameters from ISO 25178-2 are listed in Table 2. [26]

Table 2. Standard areal surface texture parameters of ISO 25178-2 [26]

Field	Sp Sv Sz St Sa Sq Ssk Sku Str Sal Std
Feature	Spd Spc S5p S10z Sha Sda Shv Sdv
Functional	Smr Sdc Smc Sxp Sk Spk Smr1 Smr2 Spq Smq Vm Vmp Vmc Vvc Vw

Substrate surface roughness tells how easily a coating material can level on the surface, and the coating surface roughness tells how well a coating material has leveled on the surface. Table 3 shows different parameters of surface roughness described in different standards. Different profilometers can measure different roughness and surface values.

Table 3. Roughness parameters described in different standards [27] [26] [28]

Parameter	Description	Standard
Ku	Kurtosis	ISO 4287, DIN 4762
r	Average radius of curvature of peaks	ISO 4287
R_a	Roughness average	ISO 4287, DIN 4768, BS 1134, ANSI B46.1
R_k	Core roughness depth	DIN 4776
R_p	Mean peak height	DIN 4762
R_{pk}	Reduced peak height	DIN 4776
R_q	RMS roughness average	ISO 4287, DIN 4762
R_v	Mean valley depth	ISO 4287
R_{vk}	Reduced valley depth	DIN 4776
R_y	Maximum roughness depth	ISO 4287, DIN 4762, BS 1134
R_z	10 points height	ISO 4287, DIN 4762, BS 113
R_{3z}	Mean third highest peak-to-valley height	DB 31007
S	Mean local peaks spacing	ISO 4287
S_m	Mean peak spacing	ISO 4287, DIN 4762, BS 1134
$\Delta\alpha$	Average profile slope	ISO 4287, DIN 4762
Δ	Comprehensive ratio of roughness ($\Delta=R_y/r$)	ISO 4287

In addition to experimental analysis methods, Eres, Weidner and Schwartz have studied mathematical modelling and simulations of the effects of surface tension gradient to leveling of evaporating multicomponent fluid. Their study presents mathematical model of a drying paint including one volatile and one non-volatile component on a 2D horizontal substrate. The model considers effects including spatial and temporal variation in evaporation rate,

lateral diffusion, viscosity, the effect of compositional changes on surface tension gradients, and coating thickness variations. [29]

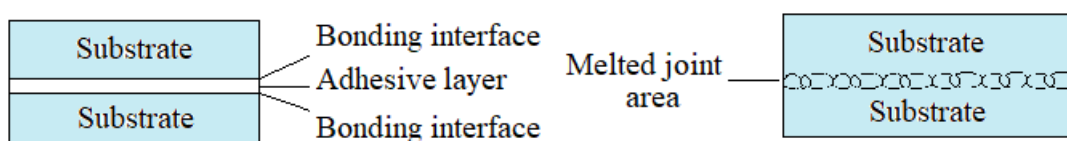
4. IMPROVING OF ADHESION

There are several ways to enhance adhesion of coating to plastics, and considering the coating material, substrate material and its surface structure, and their reactions together with the environment is important. Considering the effect of coating materials to adhesion means taking into account the coating mixture composition, dry polymer structure, solvent, and additives.

Adhesion can be improved with an additive, an adhesion promoter or bonding agent, which is a chemical added to the coating mixture. Adhesion promoter can work for example as a mechanical interlocker to the substrate. [10] Adhesion promoter can increase the coating materials affinity and the materials readiness to form bonds. Generally, additive chemicals used as adhesion promoters are divided into four categories: organofunctional silanes, organometallic compounds, chlorinated polyolefins, and a group of phosphates, silicones, and others. General formula of organofunctional silanes is $R-SiX_3$, where R refers to an organic group (methoxy, ethoxy, ethoxymethoxy etc.) and X refers to another functional group (amino, acrylate, chloro, epoxy etc.) attached to the central Si atom. The R group usually attaches to the organic coating resin and the X group to the substrate. Through hydrolysis of an X group, a silane is formed, and further a siloxane bonding between substrate and adhesion promoter takes place. This hydrolysis requires water which comes from either humidity or water-based coating material. There can be synergy achieved by using organometallic compounds together with organofunctional silanes as an additive system to improve adhesion. General composition of organometallic compound as adhesion promoter is $X-OR'-[M]-(OR)_3$. M refers to the metallic central atom, usually zirconium or titanium, having hydrolysable alkoxy or neoalkoxy chain $-OR$, an hydrocarbon chain $-OR'$, and a functional group X. Commonly amino, carboxy, and methacryloxy groups are the functional group X in these organometallic compounds. Organometallic compounds can work also as catalysts, and due their high reactivity towards hydroxyl groups, carboxylic acids, amines, and amides to form stable bonds, they enhance crosslinking and so may also accelerate curing in some coating compositions. Chlorinated polyolefins are recommended adhesion promoters for a solvent-based coating material for untreated polyolefin substrates like polyethylene and polypropylene. They can be used as additives, but they work better as primers to treat the substrate before applying the coating. From the last group, phosphates and compounds containing phosphorus are mostly used on metal substrates. Silicon and

polymers containing silicon have reactive silanol groups, so they work similarly to the organofunctional silanes to enhance adhesion, and they work also as wetting agents. Other compounds with adhesion promoting ability are for example amides and imides for plastic surfaces. [30]

When talking about thermoplastic substrates, like PI and PMMA, if direct adhesion through chemical bonding is not working, alternatively solvent cementing or thermal welding could be a better option. Solvent cementing means addition of suitable solvent(s) to soften and melt the bonding substrate surface. When pressed together, the two softened surfaces bond while the solvent either evaporates, gets adsorbed into the bonding materials, and/or polymerizes to stay on its place to work as a cement. [6, p. 412] Thermal welding means a technique with external heating and forging. The bonding surface is heated and slightly melted, and then applied to the other surface with forging pressure. [31] Also, with thermoplastics, adhesive bonding is recommended, if bonding materials are very dissimilar, or the substrate is inert to the used solvents. [6, p. 252] Bonding due to adhesive and melted joint are illustrated in Picture 11.



Picture 11. Substrates with adhesive bonding on left, and substrates with melted joint due to solvent cementing or thermal welding on right.

Chemical and physical structure of the used substrate affects the strength of adhesion. Structures of both PI and PMMA will be reviewed later in this chapter, and how the structures affect the adhesion. Adhesive systems, including plastic substrates with a polymer coating, can have a property called thixotropy, meaning thinning when isothermal agitation is applied, followed by thickening while at rest. [6, p. 413] Adhesion can be improved by minimizing internal stresses via the thixotropic effect during polymer coatings formation. [10]

In substrate surface consideration, several different surface treatment techniques can increase adhesion. For example, corona discharge works similarly to plasma treatment by improving surface energy and adhesion strength by introducing polar groups including oxygen, and irradiation treatment works by increasing the polymer surface wettability,

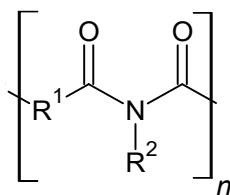
resulting improved adhesion. However, the two most common surface treatment techniques are chemical and plasma treatment. The objective of the chemical surface treatment is to modify the present chemical structure or introduce a new one to achieve new chemical or functional groups at the adhering interface. Among other chemical treatments, primers based on a solvent, like toluene and xylene, can be used as a pre-treatment to improve polymer adhesion, though by-products of some solvents, like toluene and xylene, are a chemical hazard. [10] Solvents like isopropanol are less hazardous. They enhance adhesion either by increasing surface polarity or inducing other chemical changes favouring adhesion at the surface. Some solvents could also offer a cleansing effect to the surface treated with them. Organosilanes are commonly used in adhesion promotion for their affinity to hydroxyl and other functional groups when attaching a polymer and an organic surface. [10] Different plasma techniques are commonly used to treat plastic surfaces also to achieve better adhesion. Few plasma techniques and their effects to the substrate surface, and so to adhesion, will be reviewed later in this chapter. Also, different primers and their effect on the substrate will be reviewed later in this chapter.

4.1. Adhesion on PI

The structure of the PI influences adhesion of coating to substrate, and the structure and substrate pre-treatments and primers will be reviewed in this chapter.

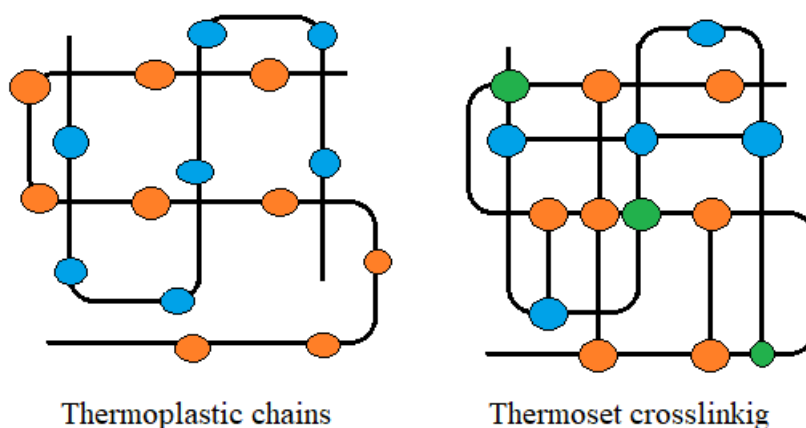
4.1.1. Structure of PI

The structure between PIs has large variety due to different functional groups, aromaticity, and polymer backbone linearity. Polyimides are made of imide units consisting of two acyl groups, C=O, bonded to nitrogen. General structure of linear PI is presented in Picture 12. Continuing structure from R¹ and R² can vary widely between different polyimides, because polyimides are derived from different dianhydrides and diamines. If both are aliphatic or aromatic, the PI is aliphatic or aromatic, respectively. If one dianhydride or diamine is aliphatic and the other is aromatic, the PI is called semi-aromatic. [7]



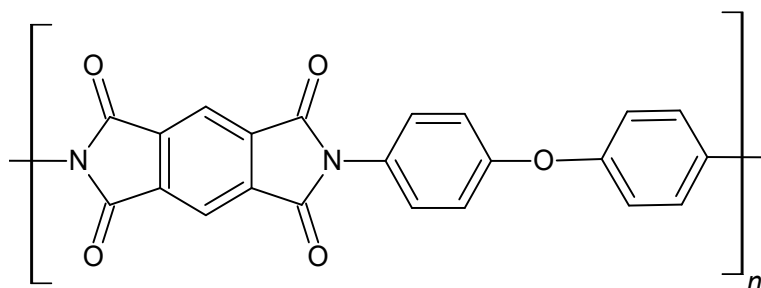
Picture 12. General structure of a linear polyimide.

Some PIs are condensation polymers forming linear structure close to thermoplastic structures, and they do not undergo chemical change when moulded. On the contrary, some PIs are more crosslinked and so thermosetting, and they undergo chemical change to be moulded. [6, p. 121] Thermoplastic PIs are tough with good strength against impact, but thermosetting PIs exhibit inherent brittleness. [6, p. 187] Picture 13 illustrates the loose thermoplastic structure, where chains can move when heated, compared to a crosslinked rigid thermoset structure, which cannot be reshaped even if heated. The effect of heat on each different PI structure should be considered during coating process if thermal curing is used. Surface structure can have great variety between different PIs.



Picture 13. Loose thermoplastic chains and rigid thermoset.

Though thermoplastic structure can move easier with heat than thermoset, generally polyimides are famous of their extraordinarily high heat-resistance compared to other polymer materials. One example used in aerospace industry is PI called Kapton®, by DuPont™. Structure of Kapton is shown in Picture 14, and it is used as substrate in some examples of adhesion improvement later in this chapter.



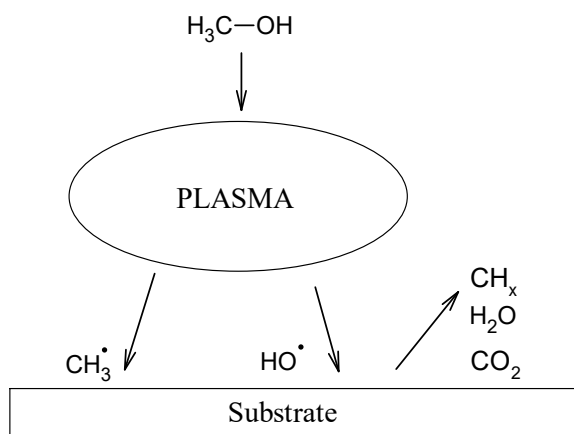
Picture 14. Structure of poly oxydiphenylene pyromellitimide -unit, commercially Kapton.

Different copolymers can also be used to modify the performance and surface structure of polyimides. In fact, siloxanes have been studied also as a component of the polyimide substrate itself. In study of Oktay, Toker, and Kayaman-Apohan, aminopropyl terminated polydimethylsiloxane was copolymerized with 4,4'-oxydianiline and 3,3',4,4'-benzophenone tetracarboxylic dianhydride before imidization by creating an electrospun mat. Siloxane content was studied in two stages, 10 mol% and 20 mol%, with two different siloxane molecular weights, 1 000 g/mol and 2 500 g/mol. Electro spun polyimide-siloxane mat was characterized with SEM and detected to have superhydrophobic nano-structure surface. Highest water contact angle achieved was $167^{\circ} \pm 2$ with 20 mol% of 2 500 g/mol polysiloxane. Thermal stability of the copolymer showed a small increase when siloxane content was decreased. [32] Though WCA and easy-to-clean effect are at significantly better level with the polyimide-siloxane copolymer, other mechanical properties like toughness or abrasion resistance of the surface were not measured, so the performance of the copolymer cannot be compared in aspects of mechanical durability to siloxane polymer coatings on PI introduced later in this thesis.

4.1.2. Improving of adhesion on PI

The main point of the Thesis is to concentrate to find ways to enhance adhesion between siloxane coatings and polymer substrates. Different pre-treatments can affect the substrate surface. For example, plasma treatment is used to clean, activate, and modify the surface properties to be more favourable for adhesion. Removing contaminants from the surfaces is important for achieving strong adhesion. Among other impurities, oils and greases can cause poor adhesion by forming boundary layer onto the substrate, preventing both mechanical coupling and chemical bonding. [10] Polymer surfaces, including PI and PMMA, can be treated with different plasma types including different gases. Different plasma types are for instance radio frequency, dielectric, and UV plasma, and they can operate either in vacuum or at atmospheric pressure with different gas mixtures, air, or ozone. Plasma can refine surfaces of polymers through etching, activation, and cross-linking, which can improve adhesion of the coating on the polymer surface. Gas or vapour type and other plasma parameters such as radio frequency/dielectric/UV power, gas flow, pressure, and treatment time should be adjusted to maximize adhesion promoting effects and to minimize surface degradation and ageing effects (post-reactions) on the chosen polymer surface. Polymer surface degradation occurs with radicals or ions in a fast interaction. Gas types commonly used in plasmas for plastic substrates are argon, nitrogen, and oxygen, alone or in mixtures.

[33] Degradation rate by plasma is assumed to be affected by the radical mobility within the substrate structure. A polymer having a higher melting point might have higher steric hindrance level resulting in lower mobility of radicals and so a lower rate of degradation, but more data is required to verify this assumption. Picture 15 shows an example of methanol vapour plasma's effect on a polymer substrate. Methanol vapour in plasma phase is divided into CH_3^\bullet and OH^\bullet radicals. The substrate surface can be damaged and different hydrocarbons, water, and carbon dioxide are released. [34]



Picture 15. Methanol vapour plasma's effect on a substrate surface. [34]

The polarity of a PI prevents adhesion, but plasma creates new active hydroxy groups to the surface that react with the coating. In study of Kwanchan Chansomwong et al., oxygen plasma was used to introduce hydroxyl groups. Other example of plasma's effect on polyimide film substrate was presented in study of Myers and Chen. Their molecular structures were studied with sum frequency generation, at the interface of PI/air and at buried interface of epoxy adhesive layer, which was attached on the PI system. Both untreated and plasma treated samples were studied and compared. SFG showed two peaks, the coupled $\text{C}=\text{O}$ imide ring's asymmetric and symmetric stretches. The relationship of those peaks tells about the imide rings tilting and angle relative to one another in the polymer backbone, so those peaks were followed throughout the study. The comparison of untreated PI films with and without epoxy adhesive showed that the molecular structure of PI was altered already by the epoxy introduction, even before plasma treatment: chemical interaction with the epoxy adhesive induced reorientation of the carbonyl groups of the imide backbone. Samples of PI were then exposed for 10 s to oxygen or argon plasma, and epoxy was added to half of the samples. There were no large spectral differences considering imide ring tilting whether oxygen or argon treatment was used after inspection of PI/air and PI/epoxy interfaces.

However, plasma treatment altered the molecular structure by decreasing the imide ring twist angles at buried PI/epoxy interface and increased the polymer surface energy, which helps wetting and adhesion. [13] [35]

Primers or chemical pre-treatment for PI wetting for $\text{SnO}_2/\text{SiO}_2$ coatings against atomic oxygen was studied with γ -aminopropyltriethoxysilane (APTES) and different NaOH concentration. Especially, alkali solution and solvents can dissolve polyimide. Desired surface properties without altering bulk properties can be achieved using NaOH pre-treatment due introduced hydroxyl groups. Better wetting of PI substrate led to better adhesion. [36] Kwanchan Chansomwong et al. prepared fluorosilane-treated hard coating of epoxy-siloxane hybrid on colourless PI. They used oxygen plasma to pre-treat the PI before adding the hard coating of epoxy-siloxane resin, called Flex 9H from Solip Tech Company. The fluorosilane, Daikin UD509, was used as friction-reducing agent and was added as the outer surface. Prior to the fluorosilane coating, they added hydrolysed tetraethoxysilane (TEOS) as a primer to improve adhesion of the fluorosilane to the epoxy-siloxane hard coating. [37]

When considering the environmental effect on siloxane coatings on PI, Shuwang Duo et al. studied degradation of siloxane coating under atomic oxygen (AO), using PI as substrate. They implanted Si ions onto siloxane coating with plasma immersion ion implanter. Their SEM and XPS results implicated that implanted Si ions under AO formed a SiO_2 layer, protecting the siloxane polymer. Small mass change was detected in mass measurement when Si implanted sample was exposed to AO, but then the mass was stabilized. Atomic oxygen erosion factor decreased by more than two orders of magnitude from the uncoated PI film to siloxane coated and Si implanted sample, and erosion factor decreased more than one order of magnitude from siloxane coating to Si implanted sample. Duo et al. concluded that implanted Si layer significantly inhibits the degradation and erosion of siloxane coating on PI in AO environment. [8]

In similar study against AO erosion, Kai Liu et al. used siloxane polymers as pre-treatment and primer layers to improve adhesion of $\text{SnO}_2/\text{SiO}_2$ coating made by sol-gel method onto Kapton PI. In the sol-gel method, a solid coating is made from small particles, colloidal solutions referred to as sol, which works as a precursor for the gel formed from a polymer or another integrated network. The pre-treatment was done first with different NaOH concentrate soaks and continued by using EtOH solution of silane coupling reagents γ -

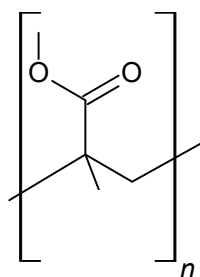
aminopropyltriethoxysilane (APTES), γ -(methacryloyloxy)propyltrimethoxysilane, or γ -mercaptopropyltriethoxysilane. Then they continued adding primer organic layer with dip coating onto PI with colloidal solution of TEOS and dimethoxydimethylsilane, and another primer layer, after drying, with colloidal solution of TEOS and methyltrimethoxysilane before dipping the substrate into the main coating $\text{SnO}_2/\text{SiO}_2$ mixture. The best results were achieved with APTES as a silane coupling agent. [36]

4.2. Adhesion on PMMA

Usually, solvent cementing and thermal welding are used for coating PMMA to acquire a stronger joint compared to adhesive bonding. Used adhesives with PMMA are second-generation acrylics, cyanoacrylates, and epoxies. All of these provides proper adhesion, but weak resistance against thermal ageing. [6, p. 252] The structure of PMMA influences adhesion alongside with coating structure, and they both will be reviewed in this chapter.

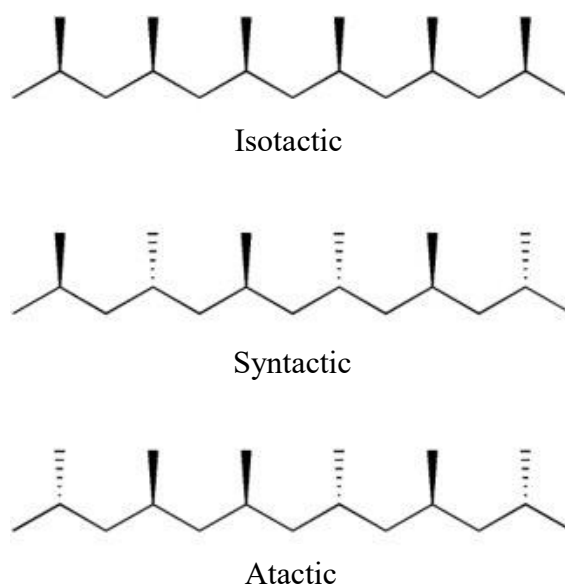
4.2.1. Structure of PMMA

PMMA's structure is a sum of polymer composition, tacticity, and production method. Pure poly(methyl methacrylate) consists only of repeating methyl methacrylate -units, shown in Picture 16, but many commercial PMMA grades are polymerized with comonomers other than methyl methacrylate. [9] Chemical structure of the surface of course varies if monomers other than methyl methacrylate are used.



Picture 16. Methyl methacrylate -unit.

PMMA was one of the first polymers studied in depth for tacticity using proton NMR. [6, p. 41] PMMA's tacticity tells the positioning of the methyl methacrylate units in polymer backbone. Different tacticities are illustrated in Picture 17.



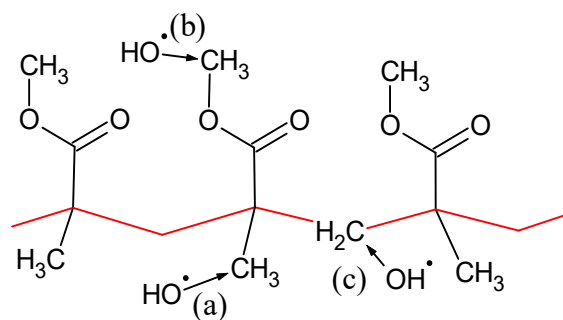
Picture 17. Iso-, syn- and atactic chains. [38]

Commercial radical polymerized PMMA is usually atactic, but often contains racemic adjacent structural units called diads, so that properties are close to those of syndiotactic. [9] [38] Properties of both syn- and atactic PMMA differ highly from isotactic PMMA's properties. [38] ToF-SIMS measurements have shown that in isotactic PMMA, the functional groups tend to turn inwards, away from the surface. Syndiotactic does not have this tendency [39], leading to conclusion that surfaces with different tacticity differ also in their surface reactions, though commercial grades are usually atactic.

4.2.2. Improving of adhesion on PMMA

The main point of the Thesis is to concentrate to find ways to enhance adhesion between siloxane coatings and polymer substrates. Plasmas effect in general was discussed more detailed on page 22.

PMMA has several sites where radicals, formed by plasma, can attack. Hydrogen atom at the methyl group, either in the methyl side group (a in Picture 18) or the methyl ester side group (b) can be abstracted. This, continued with several radical rearrangement, can lead to main chain scission. Main chain or polymer backbone is marked with red colour in Picture 18. Another H atom abstraction site for radical is the $-\text{CH}_2-$ group in the PMMA polymer backbone (c). This abstraction may lead to a $-\text{CH}-$ radical, which can cause direct radical rearrangement with scission of a C–C bond with this newly formed radical C. The key components for polymer degradation in several environments are the similar radical chain reactions. [34]



Picture 18. Radical attack sites in the PMMA chain. [34]

In the study of Hall et al., alcohol plasmas (methanol, ethanol, propanol, and butanol) on PMMA enhanced the adhesion of a siloxane coating, though argon and nitrogen gases and water vapour were also tested. [40] They cleaned PMMA samples for five minutes with methanol in an ultrasonic bath and dried with nitrogen stream prior to plasma treatment. Plasma with different alcohol vapours were effectively etching PMMA by creating hydroxyl radicals, resulting in better adhesion. Water plasmas can also etch PMMA surfaces, but they do not enhance adhesion. To achieve good adhesion, there is a certain level of etching required. Plasma can also be used to deposit thin coating layers, and pre-treatment with different alcohol vapours were found to etch but also deposit a carbonaceous layer. This thin deposited carbon-rich layer seems to enhance adhesion of a $\text{SiO}_x\text{C}_y\text{H}_z$ layer to PMMA. Water plasma did not lead to a significant formation of polymer deposition, and so did not enhance adhesion. This thin deposited layer can reduce the interfacial stress caused by differences in mechanical composition between the substrate and the added coating, and so reduce adhesion failures. [40] [34]

Dorranian et al. studied the effect of plasma treatments on pristine PMMA substrates. Table 4 shows surface energy and WCA measurements after different treatment times either with N_2 or O_2 plasma on a PMMA substrate. At up to eight minutes of plasma treatment, the nitrogen plasma provides higher and increasing surface energy compared to oxygen plasma, but after a ten minute treatment time, the surface energy drops with the nitrogen plasma, and oxygen plasma has a slightly higher surface energy. The data shows that with nitrogen plasma, the polar interaction component increases, and values have great variation whereas the dispersion component values vary little. With oxygen plasma treatment both overall surface energy values and components values variation is small. [20]

Table 4. Surface energy and water contact angle of N₂ or O₂ plasma treated PMMA [20]

Treatment time, min	N ₂ plasma				O ₂ plasma			
	WCA, °	γ_s , mN/m	γ_s^p , mN/m	γ_s^d , mN/m	WCA, °	γ_s , mN/m	γ_s^p , mN/m	γ_s^d , mN/m
0	76.30	45.76	4.40	41.36	76.30	45.76	4.40	41.36
2	33.70	68.89	25.11	43.78	40.40	62.34	24.65	37.69
4	40.70	62.40	24.16	38.24	40.80	62.04	24.52	37.52
6	21.20	73.07	32.07	41.00	43.60	61.43	21.85	39.58
8	23.60	72.09	31.26	40.83	50.10	57.29	18.38	38.91
10	55.40	52.77	16.34	36.43	52.70	55.34	17.22	38.12

Coating method can also affect adhesion because of coating film variation. Using plasma deposition as a coating method, thin coating layers can be deposited by plasma enhanced chemical vapour deposition (PECVD). When using PECVD, the film can be coated gradually by changing the oxygen flow, so that the film composition is more organic close to the interface with the substrate, and more inorganic close to the outer surface. Gradual composition leads to different mechanical properties through the film, so that softer, polymeric-like inner part has mechanically better compatibility with the substrate interface, which should ease interfacial stress and so increase adhesion. The harder surface contributes to better mechanical performance of the outer face. [34] PECVD method itself increases adhesion of this gradually layered coating, but it can be further improved with propanol vapour plasma pre-treatment. This process also increased the coating's mechanical hardness, probably due to increased crosslinking from increased number of hydroxyl groups, verified with ATR-FTIR, AFM and XPS results. It was found that pre-treatment process left residual hydroxyl groups which then incorporated into the coating while growing. [41]

In the study of Juhua Ou et al., polysiloxane coating was fabricated on PMMA substrate by sol-gel method. They tested seven different siloxane polymer composition with varying amounts of TEOS, methyltrimethoxysilane (MTMS), phenyl trimethoxysilane (PTMS) and γ -(2,3-propyleneoxide)propyltrimethylsilane and γ -(methacryloyloxy)-propyltrimethoxysilane. TEOS amount was varied from 42% to 56% out of total polymer composition. There was one test material with only MTMS and TEOS, and one with only PTMS and TEOS, and the others had equal amounts of MTMS and PTMS with varying ratio to TEOS amount. Best adhesion results were achieved with the lowest TEOS content. Adhesion of higher TEOS content samples were poor, so adhesion was improved by

reducing TEOS amount and increasing MTMS and PTMS amount. TEOS have showed tendency to form dense and highly crosslinking SiO₂ structure during curing process, which contributes to harder surface. Nonetheless, too high TEOS content is disadvantageous to film formation, and the polycondensation causes large internal stresses which affect the adhesion and lead to cracking. Compared to TEOS, MTMS and PTMS have CH₃ groups which decreases internal stresses. Adhesion with higher TEOS content (48%) was improved from poor to good with addition of either γ -(2,3-propyleneoxide)propyltrimethylsilane (KH560) or γ -(methacryloyloxy)propyltrimethoxysilane (KH570). There were no significant differences in adhesion between these two. All the material compositions are collected in Table 5 alongside adhesion results. In the crosscut adhesion test, they used ASTM standard D 3359-87, where number 1 refers to good adhesion without failure, 2 to some failure, and 3 refers to poor adhesion. [42]

Table 5. Material composition and adhesion results [42]

Composition	TEOS, g	MTMS, g	PTMS, g	KH560, g	KH570, g	Adhesion
MT2	100.00	110.00	-	-	-	2
PT2	100.00	-	110.00	-	-	2
PMT1	100.00	40.00	40.00	-	-	3
PMT2	100.00	55.00	55.00	-	-	2
PMT3	100.00	70.00	70.00	-	-	1
PMTE	100.00	53.35	53.35	3.30	-	1
PMTA	100.00	53.35	53.35	-	3.30	1

Primers are used also on PMMA, as on PI, and on PMMA primers can also be used when bonding two substrates. In study of Kim, Park, and Yang, PMMA and polydimethylsiloxane (PDMS) substrates were attached together. For the PMMA substrate, oxygen plasma was used as a pre-treatment, and then dipping in 85 °C APTES as priming. After these steps, corona discharge was used for both primed PMMA and PDMS prior to attaching the substrates. [43]

The effect of X-ray radiation has been studied in aspect of polymer degradation. The damage to polymers due to radiation can be caused by crosslinking or by bond scission in the main chain, the side-groups, or both. Dominant mechanism of PMMA damage is scissioning in both electron damage studies and soft X-ray irradiation studies, though there can also occur crosslinking in PMMA under large irradiation dosages. In the study of Piao, Fairley and

Walton, scissioning resulted in the loss of the PMMA's ester side group, and further to crosslinking and most likely forming a C=C bond. In their study, about 0.2 μm thick organic siloxane interlayer was deposited to improve adhesion on PMMA before depositing two about 2 μm thick inorganic-organic hybrid hard coating layers. Deposition was done by expanding thermal plasma deposition with varying oxygen content. Use of XPS imaging analysis to these samples provided opportunity to investigate also X-ray damage on PMMA. Adhesion of the samples was tested with tape test using crosshatch, and the crosshatch markings were studied with XPS imaging on both coating side and substrate side. In the areas where the coating seemed to be peeled off, Si was still present on the surface, so the conclusion was that adhesion failure was in the interface of the coating and PMMA and not inside of bulk PMMA. Observed C=C moieties were probably due to degradation of PMMA under X-ray radiation rather than coating deposition. The loss of ester groups was detected after the adhesion test, so the PMMA degradation should not have affected the adhesion and the test result. [44]

5. IMPROVING OF LEVELING

It was revealed during this Thesis project, that there is a limited amount of studies concerning the leveling of siloxane polymer coatings when using specifically PI or PMMA as the substrate. This led to a more general viewpoint for improvement of leveling in the following pages, including a more detailed coating method effect study. In general, there are several ways to enhance leveling of a coating onto a plastic, and considering the coating material, substrate material and its surface structure, and their reactions together is important. Considering coating materials effect on leveling means taking into account the effect of coating mixture composition, wet and dry polymer structure, solvent, and additives.

Most common industrially used leveling agents as additives such as polysiloxanes with long chains. For example, polydimethylsiloxanes work as additives as-is, or they can be modified by the addition of alkyl or polyether side chains. Crosslinking of leveling agents into the coating can also be improved with functional groups like isocyanates, hydroxyl and acid groups, or double bonds. Also, polyacrylate additives improve leveling and material flow with their low surface tension. Some of (meth)acrylic monomer-based additives are effective air-release agents. Perfluoro-modified polyacrylates work by reducing surface tension and improving substrate wetting. [16]

Wang et al. studied leveling of fouling control coatings on ship hulls with different additives and solvent mixtures. [17] They then continued to study solvent evaporation and expanded their leveling studies to non-Newtonian liquids. [25] Additive changes in their first study included silicone additive (polydimethylsiloxane), a silicone surfactant (a polyether-modified polymethyl-siloxane) as leveling additive, and an agent for dispersing and wetting (salt of phosphoric acid -groups containing polymer). Because leveling starts immediately after applying the coating material, it is crucial to observe the sample instantly to understand the phenomenon completely. [17] In the study of Wang et al., their profilometer was connected to the coating application stage. Solvent changes were made so that 20, 21, or 22.5 w-% of one solvent system of xylene was replaced with methyl isobutyl ketone to form two solvent system. Both solvent mixture changes of this scale and 2% additive changes were insignificant to the resulting film leveling and uniformity, probably due to the high viscosity of coating material itself. Significant difference in film waviness was achieved with spiral applicator instead of a flat applicator used to spread the material at the beginning. The coating formation can be influenced also by vertical force applied and application speed.

The impact of applied vertical force was studied but it was insignificant to waviness profile in respect of experimental uncertainty. The impact of application speed was also tested, and the resulting that impact was insignificant to waviness profile values. Nonetheless, they identified three different leveling stages. Immediately after coating application, the evaporation rate is constant and dominates leveling by external solvent mass transport resistance. Solvent diffusion starts dominating later when evaporation rate declines. The final stage is when heights of peaks and valleys of the film layer enhance for a moment and then start to decrease. They concluded that most probably viscosity increase due to solvent evaporation caused these three leveling stages. [17]

The following study of Wang et al. came to the conclusion that the initial average film thickness and sinusoidal wavelength were significant to the final performance of leveling. Better film leveling performance was achieved with a thicker wet film, lower coating viscosity, and shorter wavelength on application. [25]

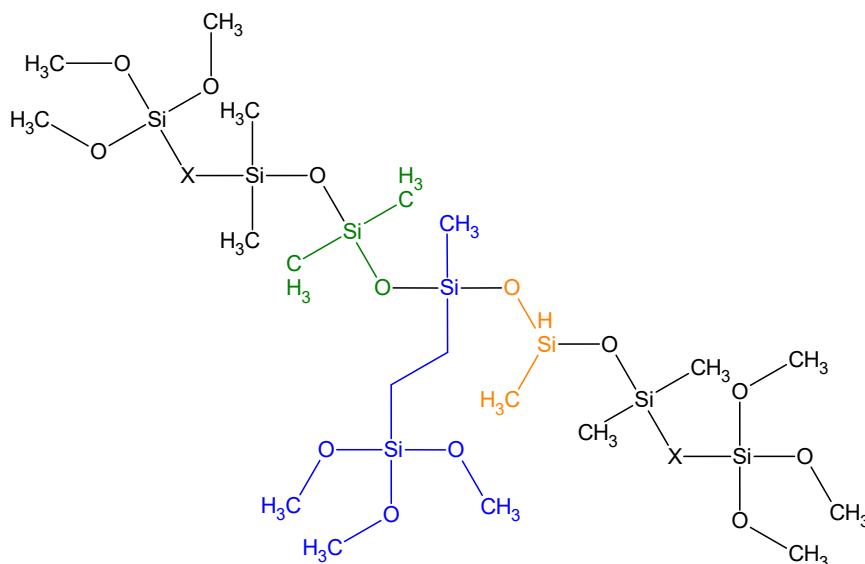
5.1. Controlled leveling

Leveling can be controlled among other things by using different components to alter the coating structure or using electrohydrodynamic forces to drive the leveling's direction. Also coating method affects material spreading and leveling.

The orange peel effect (shown in Picture 3) that occurs especially during spray coating of the substrates, can be altered with spray parameters and liquid material composition. Adjusting the air/liquid ratio and pressure on spray coating process can lead to better visual quality. On the compositional side, liquid viscosity and surface tension are critical. Liquids with lower surface tension result in smaller droplets even with same spray parameters, and single drop flow is increased. Lower surface tension can also minimize the appearance of the Bernard cells. [16]

Alongside the substrate type, also the structure of coating material affects leveling. Kim, Cho, and Lee examined a siloxane coating material and its flow and leveling properties during the process of protecting a printed circuit board. In their study, the substrate was conjunction of metal wires of connectors and chips in gaming controllers by Performance Designed Products®. However, their study showed that leveling and flow of siloxane coating material can be controlled by varying the amount of the multi-dimensional siloxane base polymers. They started their study by synthesizing four different branched or terminal-

functionalized siloxane base polymers and mixing those in varying ratios. Diameter of the spread liquid layer was tightly correlated with the percentage of trimethoxysilyl-branched siloxane base polymer in the composition, which implies that leveling and flow properties can be controlled by adjusting the formulation ratios of branched and terminal-functionalized siloxanes. Linear siloxane polymers were also synthesized with similar viscosities to those coating materials based on trimethoxysilyl-branched siloxane, to compare properties of flow and leveling with multi-dimensional networked siloxane. General structure of the siloxane polymer used in their study is shown in Picture 19. Even though the viscosities were similar, flow distances were much longer than of those including trimethoxysilyl-branched siloxane, and it was harder to control leveling or flow of linear siloxane coatings. [5] Probably, the substrate affects the leveling in this study, but leveling controllability by coating material structure could work also on plastics.



Picture 19. Siloxane polymer structure used in study of Kim, Cho, and Lee. [5]

In the study of Kim, Cho, and Lee, the siloxane polymers had varying number of functional groups to adjust for having branches or not and how high the molecular weight was. There were from 4 to 1 000 $\text{SiO}(\text{CH}_3)_2$ -groups (green in Picture 19), from 0 to 5 siloxane branches (blue), and from 0 to 3 SiHCH_3 -groups (yellow). Group marked with X between two silicones was either an oxygen atom or a CH_2CH_2 -group.

Weidner and Schwartz have also studied the modelling of surfactant amounts effect on leveling. Weak surfactants may be ineffective to initial leveling rates, but with time, even with weak surfactant a plateau can be achieved. Strong surfactants can accelerate the leveling initially before the leveling rate settles. They suggest that mathematical critical values of

surfactant concentrations should be avoided in general, but the values can be useful in controlling leveling in cases like coating 3D objects with corners, used against the tendency of leveling to flow away from edges or corners leaving thinner areas. [45]

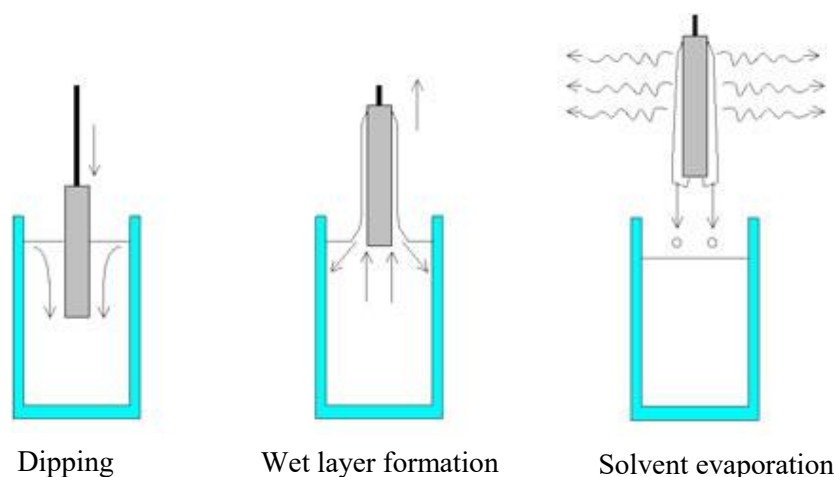
In different coating processes, electrostatic charges generated from web handling friction etc. can accumulate to substrates and liquid-air interfaces, driving liquid flows to cause defects to the coating. Static charges can attract dust particles and be a spark ignition hazard. Ramkrishnan and Kumar studied the leveling of thin liquid films under electrohydrodynamic forces. Their study took into account substrate charge distributed either homogeneously or heterogeneously, and how free charge leads to film contamination. The two forces driving leveling are gravity and capillarity. When the overall effect of forces is negative, the film levels. This occurs with high gravity number, and with large airgap, so that negative sum of gravity and capillarity overwhelms the positive electrostatic forces. The information from their study can be used to predict the parameter's impact on leveling and alter parameters towards better leveling and minimizing the number of defects. [3]

5.2. Coating methods effect on leveling

Coating method is crucial for the macro scale spreading of the coating material onto a substrate, but it also affects the micro-scale leveling of the material. Plasma enhanced chemical vapour deposition (PECVD) was introduced already at page 27; how it works as a coating method through coating growth and how it improves adhesion of siloxane coating onto PMMA. Generally, chemical vapours work by depositing layers on substrate.

Common coating methods used in industrial scale are dip, flow, Mayer rod, spin, and spray coating methods, and they will be introduced in this chapter. Siloxane polymer coatings can be applied by all these methods, and the best method should be selected so that it fits the material's viscosity and the specific application etc. to achieve the best coating performance.

In the dip coating method, the substrate is first immersed into a container filled with the coating material, then pulled out and drained before baking. Picture 20 illustrates the dip coating steps from immersion to draining. [46]



Picture 20. Steps in dip coating method. [46]

Dip coating method is a very simple method, but like the solvent evaporation step shows in Picture 20, dip coating can lead to thickness variation through the film, from a thinner top to a thicker bottom part on the substrate. Coating material viscosity affects the draining and leveling, and the solvent composition of the material affects how fast the solvents evaporate and so how long the coating takes to level. When the substrate is lifted from the immersion container and solvent evaporation starts, the viscosity of the coating increases and the leveling slows. Also, the refluxing solvent vapours above the coating material container can remove some of the coating, causing differences throughout the film. With low viscosity materials aiming to a thin coating layer, small thickness variation can be achieved because of the good draining of low viscosity materials. When aiming for thicker films with dip coating, higher material viscosity is required, and film thickness variation is harder to control.

Flow coating is introduced in Picture 21. There is continuous stream or flow of coating material applied onto the substrate, and excess material is gathered below and recirculated back to coating system. Flow coating method has similar pros and cons as dip coating method: as a method it is simple, but film thickness variation can be high because of the draining step after the material flow is stopped. The substrate is usually set vertically at an angle to improve excess material flow. The substrate can also be set horizontally, which complicates material leveling. With horizontally set substrate, the flow coating is also referred to as curtain coating, so that the material flow is perpendicular to the substrate and flows like a curtain. [47] Viscosity and target film thickness have the same effect as in the dip coating method. Other parameters to consider for avoiding film thickness variations are

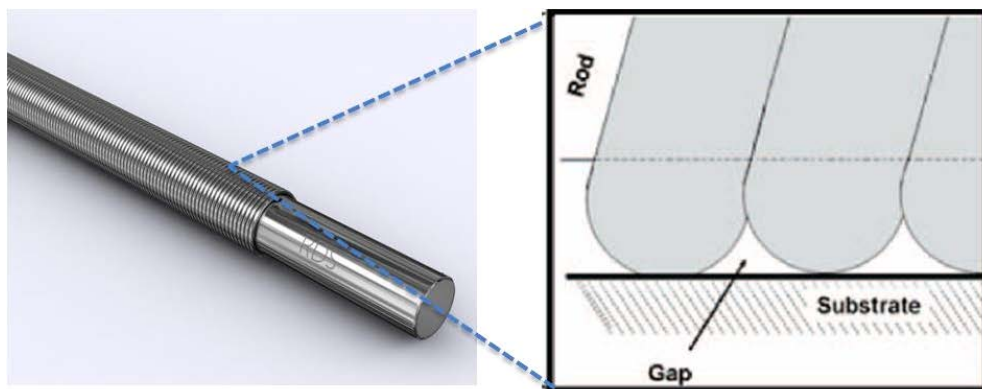
the humidity, air displacement, and the temperature. Surfactants are commonly used in coating materials to improve material flow.



Picture 21. Common flow coating process. [47]

Both dip coating and flow coating methods can be used for both 2D and 3D substrates, but in large objects the thickness variations can be wider compared to small objects.

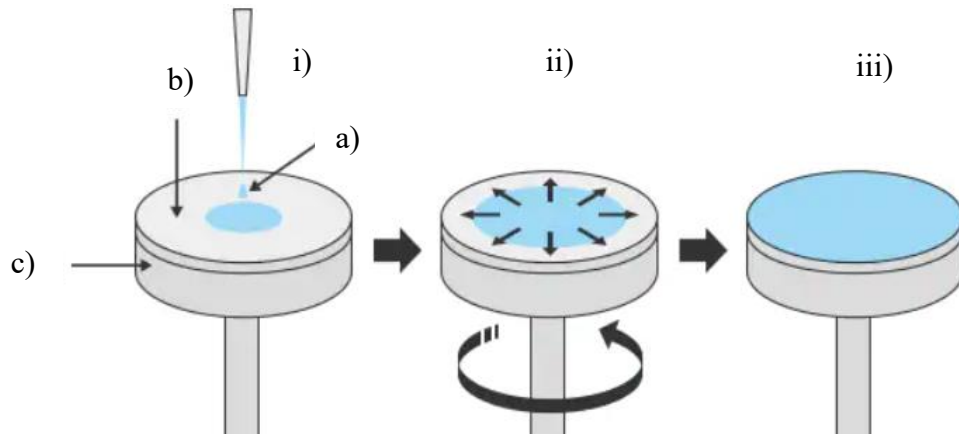
The bar coating or Mayer rod method uses a bar or a rod to swipe and spread applied coating material over the substrate. In Picture 22 i) a wire rod is presented and ii) presents a zoomed illustration of the gap between the wires and the substrate, where the coating material is left after spreading. Material and wet film thicknesses can be varied by varying the amount of applied material and varying the wire size on the rod, so that the gap size and material layer left after spreading differs.



Picture 22. Wire rod of used in Mayer rod coating method. [48]

Bar coating method can leave visible stripes throughout the coating if the material viscosity or composition does not enhance leveling after material addition or the spread layer is too thin, i.e., there is not enough material to cover all the area even when levelled.

Spin coating method is illustrated in Picture 23 where the coating material (a) is applied onto the substrate (b) which is attached to the rotating stage (c). Coating material starts to spread when the stages rotation accelerates, and centrifugal force of rotation grows significant.

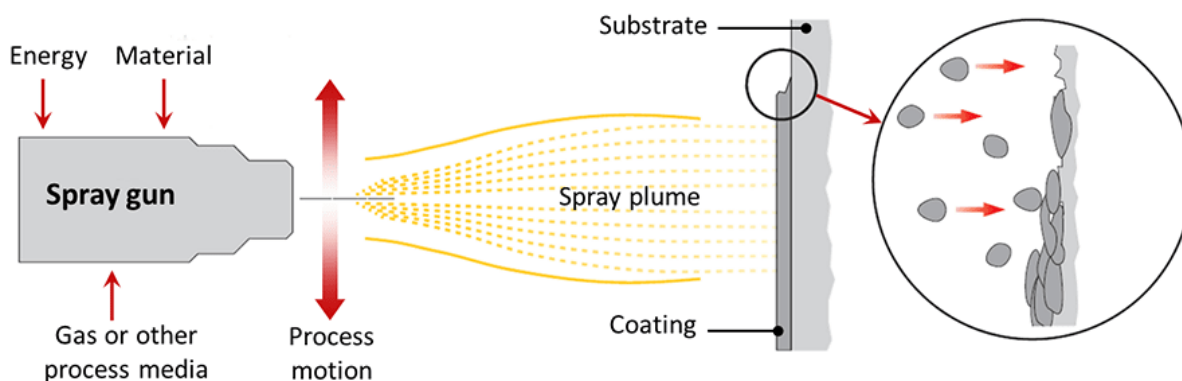


Picture 23. Illustration of the spin coating method. a) Rotating stage, b) substrate, c) coating material. [49]

In the Picture 23 ii) the arrows show that the coating material is spread to all directions due to the centrifugal force. Some leveling agents or other coating material composition adjustments might be needed to make sure there are no spiral stripes or unevenness throughout the coating before it cures. Thickness variation is also possible and should be considered in the context of leveling because the coating material is applied to a spot in the middle of the substrate where it may stick, and after spinning the film might be thicker in the middle than towards substrate edges. Disadvantage of spin coating is also the high coating material consumption due the loss of material scattered beyond the substrate when rotating.

Usually spin coating is done using horizontal rotation like in Picture 23, but also vertical rotation and vertical centrifugal force have been studied alongside with effect on surface leveling by artificial gravity. In study of Mahmoodi, Guoqing and Khajavi, vertical centrifugal force was created with rotating machine perpendicular to the silicon wafer substrate. [50] They modified traditional leveling modelling equations which lead to idea that additional gravity focused on liquid surface would reduce the amplitude of surface leveling (valleys and peaks), which they then proved experimentally. Higher artificial gravity improved surface smoothness, edge cragginess, cloudiness, and inner layer bubbling. The coating material used in their study was AZP4620 photoresist material.

The spray coating method is illustrated in Picture 24. The spray gun pushes out the liquid coating material and with gas, air, or other process media it can be shaped into an accurate plume. With plume adjustment and moving the spray gun head during coating also larger pieces can be coated precisely to have same material amount throughout the substrate. On the right in the Picture 24 there is zoomed picture to roughly illustrate the coating material droplets piling up to form a wet film. Spray plume and droplets size can be varied, usually wider plume leads to smaller droplets to enhance leveling and achieve uniform coating layer. [51] Main leveling problems with spray coating technique can occur due to wrong process parameters so that material is not applied evenly or optimally, which can lead to thickness variations through the film, or due to material viscosity, composition etc. which can lead to problems like the orange peel effect or craters showed in Picture 3.



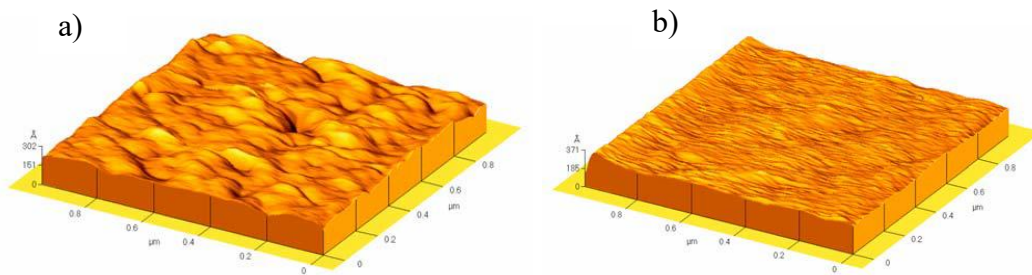
Picture 24. Illustration of spray coating method. [51]

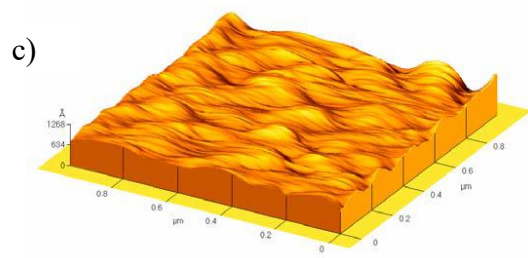
5.3. Improving of leveling on PMMA

The study of Juhua Ou et al. was introduced in context of adhesion improvement on PMMA on page 29. They fabricated polysiloxane coating on PMMA substrate by sol-gel method, and also coating roughness values were measured. Firstly, to begin with coating processes they used, the smoother coating surface was created with natural flow instead of a sponge brush coating. There were no significant uniformity issues in natural flow coated samples, whereas surfaces of the sponge brushed samples had needle-like structures in AFM study, which leads to the conclusion that with natural flow the coating material is leveled better than with the sponge brushing. Secondly, the polysiloxane material composition was affecting the surface roughness. Surface of one coating had an average roughness value of 2.79 nm, which is relatively rough. Smoother surface of another coating had an average roughness value of 2.05 nm. Material composition was almost the same in both of these

materials with 47.6% TEOS, 25.4% MTMS and 25.4% PTMS. The only difference with these two compositions was that the one with lower average roughness had 1.6% γ -(methacryloyloxy)propyltrimethoxysilane (KH570) and the one with higher average roughness had 1.6% γ -(2,3-propylene oxide)-propyltrimethylsilane (KH560). [42]

In context of leveling and surface roughness, plasma treatments with different gases have significant effects on PMMA surfaces, and so on coating material leveling. In the study of Davoud Dorrnian et al., PMMA surface was modified with O₂ or N₂ plasmas using 13.56 MHz frequency and 25 W power with different time periods. Picture 25 shows AFM graphs of PMMA surface without plasma treatment (a), surface after six minutes oxygen plasma treatment (b), and surface after six minutes nitrogen plasma treatment (c). The pristine surface has nodule like structure. The most refined surface is achieved with oxygen plasma. Nitrogen treatment modifies some of the roughness compared to the pristine sample, but surface is not then as smooth as after the oxygen treatment. Average roughness measurement was extended to ten-minute plasma treatments with both gases. The measured RMS roughness values of oxygen plasma treated samples varies randomly from initial 20 Å to 40 Å during the ten minutes period, while RMS roughness of nitrogen treated samples increases during first six minutes from 20 Å to 80 Å, almost four times higher than that of the oxygen treated. RMS roughness values of nitrogen treated samples decreases after six minutes, and after ten minutes, RMS roughness is quite the same with both O₂ and N₂ plasma. So, either of gases can be used to treat PMMA and they result with almost same roughness value, when proper treatment time is used. [20] Smoother substrate surface enhances coating leveling and wettability.





Picture 25. AFM graph of PMMA surface a) initially, b) after 6 minutes in O₂ plasma, c) after 6 minutes in N₂ plasma. [20]

6. CONCLUSION

Industrial and commercial demand of both plastics and coatings worldwide is tremendous. Both plastics and their protective or decorative coatings are used in countless everyday household and industrial applications. It is of great importance to utilize the manufactured products as long as possible and to target efforts towards prolonging product lifetimes. Coating performance on plastics is crucial to product performance and lifetime. Coating properties, e.g., adhesion and leveling, are important factors for coating performance and proper function, and when enhanced, they lead to longer product durability. The aim of this work was to introduce adhesion and leveling as phenomena, show the ways to analyse these phenomena, and find ways to improve them in coating applications and improve coating performance. The perspective of this Thesis was chosen to be siloxane polymer coatings on polyimide and poly(methyl methacrylate) substrates. Different siloxane coating applications were found from literature and reviewed, and the structures of both PI and PMMA were introduced to better evaluate the effect of substrates surface structure to leveling and adhesion.

The most common failures in material leveling and adhesion were illustrated to describe the phenomena, but several ways of improving these phenomena were also collected. Adhesion improvements introduced included techniques using different pre-treatments, primers, and additives. Pre-treatments like chemical or plasma treatments work on both PI and PMMA to activate and refine the substrate surface. Primers like TEOS and APTES are commonly used to enhance coating bonding. Different organofunctional silanes and organometallic compounds are common additives to promote adhesion.

General improvement methods for coating material leveling were also collected. It turned out to be difficult to find studies specifically about leveling of siloxane coatings on PI and PMMA, so only few ideas for those exact cases were described in this Thesis and so the aim of this work was not fully achieved. Generally, effect of leveling agents, coating methods, pre-treatments and coating material structure were described.

Environmental effect was also taken into account in the context of adhesion and siloxane polymer coatings. Polyimide is much used in aviation and space technology, and among other things siloxane coatings on PI have been studied in atomic oxygen and higher UV irradiation conditions. Siloxane coatings have shown high potential also in those applications

despite rough environment conditions. Siloxane coatings as other protective coatings are meant to have a hard surface against abrasion and scratching, especially on PMMA's relatively soft surface.

Due to the difficulties in finding literature on this topic, in future it would be interesting to see studies about different and wider variation of pre-treatments and additives used on PI and PMMA substrates having siloxane coatings.

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